Monometallic and heterobimetallic azanickellacycles as ethylene polymerization catalysts†

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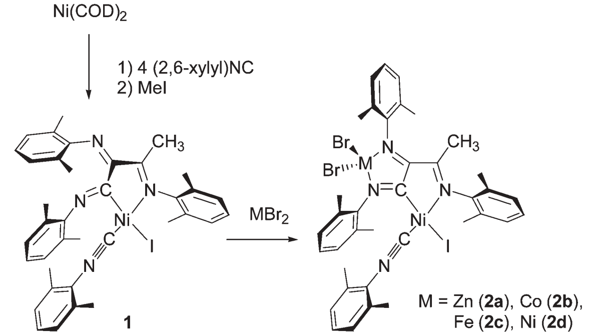
The azanickellacyclic complex (1) produced by trimerization of an isocyanide on the nickel atom is found to be a new ethylene polymerization catalyst; catalytic activity is increased by incorporation of the second metal to a diimino moiety of 1 leading to formation of heterobimetallic complexes.

Since the discovery of Brookhart's diimine–nickel complexes, nickel catalysts suitable for ethylene polymerization have actively been investigated,[1] and their excellent features have been well documented in recent articles and reviews.[2] We have recently reported a unique finding that simple Ni(II) isocyanide complexes, $NiBr_2(CNAr)_2$, behave as ethylene polymerization catalysts in the presence of methylaluminoxane (MAO), in which polyethylene of M_w = 2200 to 960000 was selectively produced by appropriate choice of the substituents on the Ar group.[3] Although isocyanides are interesting auxiliary ligands in organometallic chemistry, their high reactivity toward insertion between metal–alkyl bonds has prevented the exploration for catalysis; in particular, certain nickel salts or complexes are good catalysts for self oligomerization and polymerization of isocyanides.[4] In this sense, the catalysis of $NiBr_2(CNAr)_2$ described above is unique in metal–isocyanide chemistry; however, polymerization mechanisms are difficult to specify due to possible involvement of the isocyanide oligomerization or polymerization on the nickel atom in the generation of net catalytic species by treatment of $NiBr_2(CNAr)_2$ with MAO.

In this paper, we wish to report new polymerization catalysts which originated from our assumption that the insertion of CNAr to Ni–alkyl bonds and the resulting oligomerization of CNAr may be involved in the $NiBr_2(CNAr)_2$/MAO-catalyzed ethylene polymerization. It was reported that reaction of $MeNiCl(PMe_3)_2$ with ^tBuNC results in insertion of three ^tBuNC to form azanickellacylopentenes.[5] Similar metallacycles can be alternatively synthesized by treatment of $Ni(COD)_2$ with CNAr and MeI as reported in the literature,[6] and a modified process using CN(2,6-xylyl) resulted in preparation of the azanickellacyclopentene (**1**) in 89% yield (Scheme 1). Characterization of **1** was performed by spectroscopy (^1H, ^{13}C, IR), crystallography,‡ and elemental analysis. As shown in the ORTEP drawing illustrated in Fig. 1 (left), an imidoyl carbon, an imine nitrogen, an iodine atom, and an isocyanide ligand are bonded to the nickel center with a square-planar arrangement. Ethylene polymerization was typically performed in a 100 mL stainless autoclave fitted with a Teflon inner tube, in the presence of MAO (200 eq. to **1**) at room temperature. As shown in Table 1, entry 1, the activity reached 0.6 kg mmolNi^{-1} h^{-1} to give polyethylene of $M_w = 2.6 \times 10^5$ with $M_w/M_n = 3.3$. ^{13}C NMR of the polymer showed the existence of the methyl branch (8.3C/1000C). The $NiBr_2(CNAr)_2$/MAO catalyzed ethylene polymerization depends on the substituents on the Ar group, and $NiBr_2[CN(2,6\text{-xylyl})]_2$/MAO is not efficient among the catalysts we examined; the activity was 1.81 g mmolNi^{-1} h^{-1} and the M_w of the polyethylene formed was $M_w = 2 \times 10^5$ ($M_w/M_n = 3.3$, the methyl branch = 13.7C/1000C) under the same conditions as the **1**/MAO system. It is apparent that **1**, which is the first example of polymerization catalysts containing an azanickellacyclopentene sturucture, is 333 times more efficient than $NiBr_2[CN(2,6\text{-xylyl})]_2$.



Scheme 1 Preparation of azanickellacyclic catalysts.

An interesting structural feature of **1** is existence of the diimino substructure in the molecule. Incorporation of the second metal species to this diimine moiety resulted in formation of heterobimetallic complexes (Scheme 1). In a typical example, reaction of **1** with $ZnBr_2$ in THF–toluene gave a diamagnetic bimetallic complex **2a**, which was characterized by spectroscopy (^1H, ^{13}C, IR), crystallography, and elemental analysis. The ORTEP drawing [Fig. 1 (right)] revealed that two nitrogen atoms of the diimino substructure are coordinated to the Zn center, and the arrangement of the ligands around the Zn is tetrahedral. Ethylene polymerization by **2a**/MAO under the same conditions as described above showed the catalytic activity of 1.03 kg mmolNi^{-1} h^{-1}, which is 1.75 times larger than that by the **1**/MAO system (entry 2). Further examination of the incorporation of the second metal revealed that bimetallic complexes formed by the reaction of **1** with $CoBr_2$, $FeBr_2$ and $NiBr_2$(dme), respectively, also exhibited significantly enhanced reactivity (1.2 ~ 2.7 times larger than that of the **1**/MAO system) as shown in entries 3–5.

This significant enhancement of the catalytic activity by introduction of the second metal may be a unique entry to

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† Electronic supplementary information (ESI) available: preparation and characterization details. See http://www.rsc.org/suppdata/cc/b5/b502942b/

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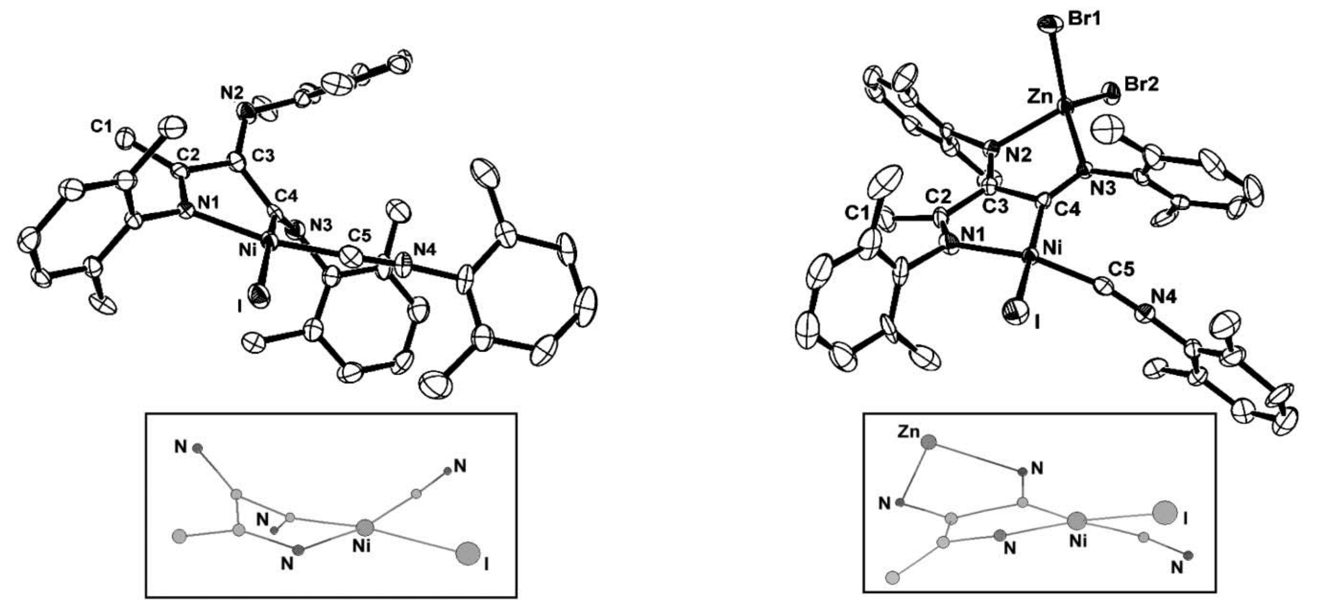

Fig. 1 X-ray structures of **1** (left) and **2a** (right).‡ Thermal ellipsoids are shown at 50% probability. Figures in squares are the nickellacycle skeletons. Hydrogen atoms (**1** and **2a**) and solvate molecules (**2a**) are omitted for clarity. Selected bond lengths (Å) dihedral angles (deg): **1**: Ni–I 2.5770(8), Ni–C(5)1.821(5), Ni–N(1) 1.969(4), Ni–C(4) 1.906(5), C(5)–N(4) 1.159(6), N(2)–C(3)–C(4)–N(3)–58.4(8), N(1)–C(2)–C(3)–C(4) 27.1(6). **2a**: Ni–I 2.481(1), Zn–Br(1) 2.394(1), N(2)–Zn 2.115(7), Ni–C(5) 1.824(9), Ni–N(1) 1.941(8), Ni–C(4) 1.863(8), C(5)–N(4) 1.16(1), N(2)–C(3)–C(4)–N(3)–2(1), N(1)–C(2)–C(3)–C(4) 12(1).

Table 1 Polymerization of ethylene by mono- and bimetallic azanickellacyclopentenes

Entry	Complex (amount of catalyst) μmol	Yield g	Activity kg mmolNi^{-1} h^{-1}	M_w	M_w/M_n	T_m °C	Branch 1/1000C
1	**1** (1) none	0.197	0.591	260 000	3.3	125.0	8.3
2	**2a** (1) $ZnBr_2$	0.344	1.032	290 000	3.3	128.1	4.2
3	**2b** (1) $CoBr_2$	0.234	0.702	280 000	2.9	128.1	4.3
4	**2c** (1) $FeBr_2$	0.540	1.620	190 000[a]	3.4	127.4	7.6
5	**2d** (1) $NiBr_2$	0.709	2.127	240 000[a]	3.6	132.9	4.4

[a] The GPC profile is bimodal. [b] All reactions were carried out in a 100 mL stainless-steel autoclave in the presence of MAO (200 eq.) based on the charged nickel catalysts at room temperature for 20 min. Ethylene (0.8 MPa) was applied.

"bimetallic polymerization catalysts", in which the second metal apparently plays an important role in the catalysis. The complexes **2a** ∼ **2d** have an α-diimine structure to which $ZnBr_2$, $CoBr_2$, $FeBr_2$, and $NiBr_2$ species are coordinated. Although the exchange of the growing polymer chain between metal and zinc center is reportedly very fast and reversible in iron-catalyzed ethylene polymerization, it is known that zinc itself has no polymerization activity.[7] In contrast, cobalt, iron and nickel potentially act as an active center for ethylene polymerization.[8] One explanation for the second metal effect is the enrolment of the structural change of the azanickellacyclopentene by incorporation of the second metal. As illustrated in Fig. 1, incorporation of $ZnBr_2$ to the diimino moiety of **1** results in increase of the planarity of the azanickellacyclopentene, and makes the ring structure more rigid; this could increase the durability of the catalyst. Similar structural change is also seen in the molecular structure of Ni/Co heterobimetallic complex **2b** as shown in the ESI†. A further and important possibility is involvement of the second metal in the polymerization mechanism. The monomodal GPC profile showing similar M_w and M_w/M_n of the polymers formed indicates that this is not probable in the polymerization catalyzed by **1**, **2a**, and **2b**. In sharp contrast, bimodal GPC profiles in the polymers obtained by **2c** and **2d** may support the enrolment of the second metal as the active center for polymerization.§ We are currently investigating this possibility in detail, as it may provide bimetallic olefin polymerization catalysts in which individual metals exhibit different polymerization behavior.

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Notes and references

‡ **1**; $C_{37}H_{39}IN_4Ni$, Fw. = 725.35, monoclinic, a = 29.374(9) Å, b = 14.767(4) Å, c = 17.319(5) Å, β = 116.5987(11)°, V = 6717.6(33) Å^3, Space Group = $C2/c$ (#15), Z = 8, μ(MoKα) = 15.28 cm^{-1}, No. of Reflections measured [total: 27045, unique: 7638 (R_{int} = 0.082)], R (all) = 0.092, $R1$ ($I > 2.00\sigma(I)$) = 0.042, $wR2$ (all) = 0.111. **2a**; $C_{37}H_{39}Br_2IN_4NiZn{\cdot}CH_2Cl_2$, Fw. = 1035.47, monoclinic, a = 15.091(2) Å, b = 11.585(2) Å, c = 22.938(4) Å, β = 97.1574(8)°, V = 3979.1(11) Å^3, Space Group = $P2_1/c$ (#14), Z = 4, μ(MoKα) = 40.33 cm^{-1}, No. of Reflections measured [total: 30715, unique: 8994 (R_{int} = 0.035)], $R1$ ($I > 3.00\sigma(I)$) = 0.055, $wR2$ ($I > 3.00\sigma(I)$) = 0.161. **2b**; $C_{38}H_{41}N_4Br_2CoINiCl_2$, Fw. = 1029.02, monoclinic, a = 15.211(1) Å, b = 11.6798(8) Å, c = 22.888(2) Å, β = 96.590(2)°, V = 4039.5(5) Å^3, Space Group = $P2_1/c$ (#14), Z = 4, μ(MoKα) = 37.90 cm^{-1}, No. of Reflections measured [total: 9201, unique: 8837 (R_{int} = 0.000)], R (all) = 0.109, $R1$ ($I > 2.00\sigma(I)$) = 0.069, $wR2$ (all) = 0.225. CCDC 198229 (**1**), CCDC 265483 (**2a**) and CCDC 265482 (**2b**). See http://www.rsc.org/suppdata/cc/b5/b502942b/ for crystallographic data in CIF or other electronic format.

§ GPC profiles of the formed polymers suggest that all of the polymers have a peak at M_p = 230,000~270,000; those obtained by Ni (**1**), Ni/Zn (**2a**), Ni/Co (**2b**) catalysts are monomodal, whereas those by the Ni/Fe (**2c**) and Ni/Ni (**2d**) catalysts are bimodal showing an additional peak at lower molecular weight regions (M_p = *ca.* 90,000). See, details in ESI†.

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